The First General Meeting was held at the Camborne School of Mines, on the 1st October, 1958. Owing to the absence of the Retiring President, Mr. L. G. Brown, Mr. F. B. Michell (Vice-President) was in the Chair. Before calling upon Dr. K. F. G. Hosking to give his Presidential Address, Mr. Michell referred to the death of Mr. E. Furze.

THE ANALYTICAL ASPECT OF GEOCHEMICAL PROSPECTING FOR METALS

by

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ABSTRACT

Analytical methods used in the course of applied geochemical studies are reviewed and their relative merits are discussed.

INTRODUCTION.

It is becoming increasingly apparent that the broad distribution pattern of ore-bodies generically related to a given batholith was already determined by the time the igneous body was being emplaced, as those cupolae around which lodes, etc., subsequently developed tend to be characterised by containing, in certain of their mineral species, higher concentrations of 'lode-elements' than are found in the same species of barren, but otherwise not obvious dissimilar, igneous masses. Thus, provided adequate analytical methods are available, this fact should enable the areas of batholithic regions which are most likely to be lode-bearing to be selected fairly rapidly. Furthermore, during the development of a primary ore-body, ore-forming agents tend to migrate into the country-rock, beyond the site of intensive deposition, and to deposit small quantities of ore-elements there. The envelope of anomalous metal concentration which is thus formed around the ore-body is often considerably more extensive than the zone of obvious wall-rock alteration. Also, pre-ore-formation fissures leading into, and away from, the site of major deposition may be characterised by containing concentrations of ore-elements, which are anomalous when compared with the adjacent rock and with the contents of fissures not connected with ore-bodies, but which cannot be established by microscopic examination.

When an ore-body is subjected to erosion, some of its components will be dispersed in the nearby soil, also in the spatially related ground and surface waters and stream sediments. In addition, variations in the trace-element content of soils may be reflected in the chemical composition of the plants growing on them.

It follows, then, that if these zones of anomalous metal concentration can be established by the analysis of soils, plants, etc., they might lead to the discovery of hitherto unknown ore-bodies, or to the confirmation of others which have been only broadly indicated by other methods of prospection. The establishment of the presence of such anomalies, followed by their interpretation, constitute the aid to mineral exploration known as geochemical prospecting.

Obviously a zone of anomalous metal concentration cannot be delineated until the normal - or 'background' - concentration of that metal in the soil (or what-

ever medium is to be investigated) of the area to be surveyed has been established. So far as rocks, and the soils derived from them, are concerned, the background values may vary markedly from one type to another: the same is true of different species of plants, and of different parts of the same species. Furthermore, the background values of plants and natural waters usually show considerable seasonal fluctuations. Often the background concentration of an element in rocks, soils, sediments and plants may be less than, say, 20 parts per million, whilst in the case of natural waters it is usually considerably less than 1 part per million.

The sample interval necessary to establish meaningful metal anomalies in soils, plant populations, etc., varies enormously, and can best be established by carrying out preliminary work - whenever this is possible - over a part of the general area to be investigated which contains a known deposit similar to those which are being sought. Frequently, however, the sampling interval must not be greater than 100 ft. and, on occasion, it may have to be as little as five.

From the above observations it follows that geochemical prospecting is only likely to be widely applied if the elements of interest can be determined cheaply and rapidly, even when they are present in exceedingly small amounts in the material to be analyzed. It is, however, important to realise that semi-quantitative methods provide a sufficient degree of accuracy for the work under review, and, furthermore, it is only necessary to establish relative, not absolute, concentrations. That is to say, a method enabling a fixed proportion of a given element to be determined would be normally quite adequate. Indeed, the most revealing results are, on occasion, obtained by determining that fraction of the element which can be extracted from the sample by a cold, comparatively innocuous attacking reagent.

Rapid, cheap, semi-quantitative determinations of the type necessary for applied geochemical work may usually be made either by employing instrument methods of analysis or by simple colorimetric methods, but as the latter are of more general interest, because they involve only a small capital outlay and so even very small companies could use them, they are given prominence in this paper. Generally, however, it is true to say that whenever a comprehensive trace element map of a region is to be prepared, or when an area is to be subjected to saturation prospecting with a view to discovering if it holds any mineral deposits of economic interest, then an instrument method of analysis should be used which is capable of yielding, simultaneously, quantitative data relating to many elements in each sample. On the other hand, colorimetric methods have much to recommend them when one, or at most a few elements are to be sought, particularly in an area of limited extent. Such a method would, for example, be ideal for tracing the extension of a copper lode. In a few instances, however, a single element, or a small group of elements which possess unusual physical properties, may be conveniently traced by employing certain special, readily-transportable instruments. Thus, the Geiger Counter and the Scintillation Meter are usually the most valuable aids to the search for radioactive elements, whilst the Beryllometer enables beryllium to be detected and determined quantitatively very rapidly - even when it is present in trace amounts - in many natural environments. However, the advantages, etc., of the various analytical methods are discussed somewhat more fully in the following pages.

TABLE I

ANALYTICAL METHODS USED BY THE APPLIED GEOCHEMIST

A. METHODS IN WHICH INSTRUMENTS PLAY A DOMINANT ROLE.

1. Capable of yielding data concerning a considerable number of elements more-or-less simultaneously.

    a. Spectrographic.
    b. Polarographic. Employing instruments differing widely in sensitivity.
    c. X-ray fluorescent spectrometric.

2. Capable of yielding data concerning a single element or only a few elements.

    a. Beryllometric.
    b. Radiometric.

3. Capable of yielding information concerning the physico-chemical state of the area of investigation.

    a. pH measurements.
    b. eH measurements.
    c. Temperature measurements.
    d. Determination of luminescence.

B. METHODS IN WHICH INSTRUMENTS DO NOT PLAY A DOMINANT ROLE.

1. Tests which may yield considerable qualitative information but only limited quantitative data.

    The Feigl-type spot tests, Short's microchemical tests, rock-face staining tests, etc.

2. Colorimetric.

    a. Involving the development of a coloured solution of a compound, or complex, of the element to be analysed, and then comparing the 'colour' of the solution with real or synthetic standards, either by eye or by means of an instrument.

    b. Involving the development of a suspension of a compound, or complex, of the element in a solution, followed by eye, or instrument, comparison with standards.

    c. Involving a preliminary separation of the element to be determined by a paper chromatographic method, followed by the development of a characteristically coloured compound, or complex, of the element on the paper, and subsequent comparison with standards.

    d. Employing a preliminary concentration of the element to be determined by collecting it on ion-exchange resin followed by some form of colorimetric analysis.

TABLE I (Continued).

e. Employing a preliminary separation involving the development of a low-boiling compound of the element, followed by its removal by distillation and subsequent determination by colorimetric means.

f. Confined-spot methods.

i. Depending on the collection, or development, of a characteristically coloured precipitate on a confined spot of filter paper, followed by comparison of the spot with similarly prepared standards.

ii. Depending on the development of a confined spot by reaction between a volatile compound of the element to be analysed and a reagent supported on filter paper.

g. Unconfined-spot methods employing standards.

Depending on the development of a characteristically coloured compound, or complex, of the element to be determined as an unconfined spot on appropriately impregnated filter paper, followed by comparison with similarly-prepared standards.

Analytical methods which are, or which may be, widely employed in geochemical prospecting are classified in Table I, and these are discussed in the order in which they occur there.

INSTRUMENT METHODS.

Spectrographic Analysis.

Spectrographic methods of analysis were the first to be used by applied geochemists during their investigations into the trace element content of plant and soil samples, and they are still the most valuable when geochemical techniques are being employed to investigate the mineral potential of a large area whose geology has not been investigated in detail.

By means of the spectrograph a large number of elements in soil, sediment, rock and plant samples can be determined simultaneously and rapidly, and during the course of each analysis a permanent photographic record of the chemical nature of the sample is obtained which can, if necessary, be re-evaluated, both qualitatively and quantitatively, in the future. The spectrographic sensitivity for most elements of interest to the applied geochemist is such that the method of analysis is admirably suited to the solution of most of his problems: zinc, however, is a notable exception. Although the absolute sensitivity of a spectrographic method is usually higher than a colorimetric one, this may be counterbalanced by the fact that a much larger sample can often be taken when using the latter. On the other hand, no simple colorimetric methods have been developed for certain elements (e.g., calsium, rubidium and lithium) which can be determined without difficulty, by spectrographic means. The constant purification of reagents (including the preparation of metal-free water) and the ever-present danger of introducing contamination if this is not carried out efficiently (which bedevils the colorimetric determination of trace-amounts of elements) are virtually absent when the spectrograph is employed. In addition, it is only necessary to make a comparatively small number of sets of standard spectrograms during the course of a given prospecting programme, whereas when colorimetric methods are resorted to it is often essential to prepare fresh standards daily. Although spectrographic results can be read visually they can be obtained instrumentally, and then they are independent of individual errors of reading. There are, however, a number of facts which militate against the general employment of spectrographic analysis. A suitable instrument (e.g., a large Hilger quartz spectrograph), together with the accessory pieces of apparatus (such as a densitometer, comparitor, refrigerator for storing film, etc.) cost several thousands of pounds, and, in addition, a further considerable sum of money must be spent in constructing an adequate air-conditioned static, or mobile, laboratory. Also, at least one experienced spectroscopist must be employed. Although mobile spectrographic laboratories have been used by the Russians, French and the Americans (Beguinot, 1956: Canney, Myers and Ward, 1957), the terrain in which they can operate is severely restricted, and in difficult country the simple colorimetric methods come into their own by virtue of the fact that the necessary apparatus and reagents can be transported, without undue difficulty, anywhere. Finally, unless a high standard of cleanliness is maintained, and a rigid operational routine is adhered to, errors of considerable magnitude can be introduced.

The rate at which results can be obtained is high and the cost is moderate. Thus, in Rhodesia, a team of four persons (a spectroscopist, an operator, a sample

preparationist and a sample crusher) operating in a well-designed laboratory, are able to determine six metals in about 5,000 samples per 20-day working month (assuming a 5-day week, 8-hour day) at a cost of 40 cents (American) per sample (Bichan, 1958, 61).

From the above it follows that in view of the high capital cost involved a company would be ill-advised to contemplate the use of the spectrograph during exploration unless it was to undertake work of such magnitude that each of many thousands of samples would, of necessity, have to be analyzed for several metals, or unless the instrument could be profitably employed in other analytical work (e.g., in the routine determination of minor elements in metallurgical products). Nevertheless, whenever a geochemical survey of reasonable proportions is contemplated, a limited number of spectrographic analyses should be made during the initial stages of the work - if it is at all possible - even though colorimetric methods are to be used subsequently, as the spectrograph may not only reveal the best 'path-finder' element but it may also establish the presence of unsuspected elements of economic importance. It seems clear that 'ere long no region will be regarded as having been adequately geologically investigated unless it has been subjected to a comprehensive geochemical survey. Thus, it is reasonable to believe that government-sponsored geological departments will, of necessity, make ever-increasing use of the instrument under discussion.

Polarographic methods.

The 'normal' polarograph is capable of rapid and simultaneous determination of a number of metals in solution. It is not a particularly costly instrument and many routine determinations may be carried out by an operator without a great deal of training, although, on occasion, interfering substances may have to be removed initially by the classical methods. Unless, time-consuming preliminary concentrations are resorted to the apparatus is not generally sufficiently sensitive for applied geochemical studies. Nevertheless, on occasion, where the instrument has been available, and the metal concentration in the soil of the area has been exceptionally high, it has been used successfully. Thus, at Broken Hill, Northern Rhodesia, it has served to determine zinc in soils, and in Japan - according to Hidehiko Mino (1955, 97), a robust polarograph, designed primarily for close mill-control, has been employed during geochemical prospecting for copper and zinc.

The square-wave polarograph is a much more versatile and sensitive instrument which may well become an important analytical tool to the geochemist who is concerned with large-scale surveys and the preparation of regional geochemical maps. As yet, however, the writer has not found anything in the literature concerning its actual employment in such work.

X-ray fluorescent spectrometric methods.

X-ray fluorescent spectrometric analysis was first employed for the analysis of soil samples in connection with geochemical studies by Adler and Axelrod (1955) and later Salmon (1958) used the method for the geochemical analysis of soil-water and plant samples. More recently Webber (1959) has reported the results of extensive investigations concerning the application of the method to geochemical prospecting, and he has used it successfully to determine zinc, iron, manganese, copper, lead and nickel in soil samples and stream sediments. The advantages

and disadvantages of the method, when compared with others, are summarised by Webber (op. cit., 818) as follows:-

"Advantages: 1. The X-ray spectrometer can be operated at a relatively low cost after it has been acquired. 2. A large number of different elements can be detected. 3. The analysis can be made quite accurate if desired. 4. The spectrum is simple to interpret. 5. Analysis can be very rapid. 6. Analysis is nondestructive and permits easy recheck of an analytical determination on the same sample.

Disadvantages: 1. Initial cost of equipment is high. 2. It is not possible to do on-the-spot analyses such as can be done with colorimetric tests. 3. Sensitivity is not as good as is desired for many elements. 4. Electronic equipment is involved and requires maintenance."

As in the case of the spectrograph, such an instrument is only likely to be employed by geological surveys and university departments which are engaged in extensive geochemical investigations, or by large mining companies who may, in fact, possess the instrument primarily for routine metallurgical analyses. It is, however, likely to be used ever-increasingly by the above groups in view of the ease and rapidity with which a determination may be effected once the appropriate analytical technique has been devised: the writer is, however, very conscious of the fact that if this instrument is to be used it is of paramount importance that an electronic engineer who has an intimate knowledge of it should always be readily available.

The beryllometer.

In order to meet the growing demand for beryllium, both instrument and colorimetric methods have been devised to facilitate the search for new sources.

The instrument (termed by some a beryllometer) described by Bowie et al. (1959-60, LXIX, 345 - 359) for use in the field weighs 40 lbs. and is carried (by means of two handles - each 4 ft. long) by two operators. It consists essentially of a 'slug' of antimony-124 which emits gamma radiation in the range of 0.6 to 2.3 MeV with a major contribution at 1.69 MeV. The characteristics of this radiation are such that if it falls on berullium-bearing material neutrons are released in proportion to the quantity of beryllium present. These neutrons are recorded by BF_3 counters and the counts are registered by an indicator unit which is clamped to one of the handles. Fuller details of the apparatus are available in the paper noted above.

Despite its weight the instrument is easy to use even in rugged terrain and is of the utmost value for the purpose for which it was designed. A beryllometric survey is carried out in the same way as a radiometric one. There are, however, three weaknesses in the method - though they are all minor ones. Firstly, there is a distinct radiation hazard; secondly, the antimony must be periodically renewed and thirdly, only beryllium which is virtually at the surface can be detected. A more elaborate laboratory model is also described by Bowie (op. sit.) which is capable of rapid and accurate determination of beryllium in a wide variety of samples. Field models can now be obtained from Messrs. Plessey Nucreonics, Ltd., Northampton, at a cost of £700.

Radiometric methods.

Radiometric surveys employing either the Geiger/Müller or the Scintillation Counter are too well known to need description here. They are usually the most satisfactory means of locating radio-active deposits although on occasion the employment of rapid chemical methods to detect uranium in soils, stream sediments and river water may prove advantageous. (See Ostle, 1954).

pH and eH measurements.

Determination of the degree of acidity (pH) and the oxidation/reduction potential of the parent material (e.g., soil, sediment, stream-water) at each sampling point by means of a portable instrument is of considerable value in that they often throw considerable light on the manner of dispersion of the metals being studied. In addition, variation in the degree of acidity of the soil may well reveal the position of a sub-outcropping actively-oxidising sulphide ore-body and so serve to confirm the results obtained by the determination of the appropriate metals.

Temperature measurements.

During the active oxidation of an ore-body a considerable amount of heat is generated and so, provided a sufficiently sensitive and portable temperature-measuring apparatus is available it should be possible to locate a sub-outcropping deposit of this type by measuring the soil-temperature at points on a grid. Nomura and Naofumi (1958) have carried out work of this nature in the vicinity of Kunitomi mine, Hokkaido, and have shown that the outcrop there exists in a relatively high temperature zone. They used an injection-type thermometer capable of measuring the soil temperature to an accuracy of 0.5 to 1.0 deg. C.

Determination of luminescence.

McDougall (1954, 717-726) has carried out studies which have indicated that hydrothermal ore-bodies are frequently surrounded by a zone of rocks possessing a degree of thermoluminescence greater than the background, and he suggests, therefore, that this fact may be used as a guide to the location of certain mineral deposits. The analytical work in connection with such studies simply involves heating specimens below a red heat in a dark room and making a visual assessment of the degree of thermoluminescence exhibited. This is not an instrument method but it is most conveniently described here and, doubtless, the method could be refined by determining the degree of thermoluminescence instrumentally.

METHODS IN WHICH INSTRUMENTS DO NOT PLAY A DOMINANT ROLE.

Tests which may yield considerable qualitative information but only limited quantitative data.

Any chemical test which is simple and quick and which is sufficiently sensitive to reveal the presence of a given element in rock and soil samples, etc., may prove of value during the search for ore, and so such tests can be legitimately discussed in a paper such as this. Indeed, Ginzburg gives some prominence to such methods in his "Principles of Geochemical Prospecting" when dealing with

methods of analytical investigations used by the Russian geochemists (1960, 1-11). Such tests, which include blowpipe analysis, contact printing, microchemical tests of the type used by Short (1940), and spot tests - particularly those devised and popularised by Feigl (1947) - are typical of those under consideration. By standardising the operations, strength of reagents, etc., a certain limited amount of quantitative data may also be obtained from such tests if the amount of precipitate formed, the time the precipitate takes to form, the depth of colour produced, etc., are evaluated. However, as many simple and reasonably precise colorimetric tests are now available those of the type noted above rarely play more than an ancillary role in geochemical prospecting and so need not be discussed further.

Colorimetric methods.

Colorimetric analysis normally involves the preparation of a coloured compound of the element to be determined, followed by comparison of the intensity or shade of its colour with those of a series of standards prepared from known amounts of the element under strictly comparable conditions. Generally it is the colour of a solution of the compound which is evaluated, but on occasion the compound is precipitated on filter paper and its colour is compared with standards similarly prepared. Often the standards have to be produced daily as many are unstable, and as this is a time-consuming process efforts have been made to replace the natural standards by synthetic ones. Hawkins, Canney and Ward (1959), for example, have been able to substitute coloured rods of plastic for a number of natural standards, whilst it has long been the practice to use synthetic standards in the form of discs of filter paper, suitably tinted with water-colours to match an initial set of natural, very unstable standards, when determining the amount of elemental arsenic precipitated in a Gutzeit apparatus during the routine determination of this element in soil samples, etc. (See Almond, 1953).

For a colorimetric method to yield meaningful results a small change in the concentration of the element being analyzed must be reflected by an appreciable change in the intensity or shade of its compound. In any such method there is a lower concentration point below which there is no apparent colour and an upper above which the colour is so dense that increases in concentration produce no obvious colour change. This working range varies markedly from method to method. The smallest amount of a given element which can be determined satisfactorily from the point of view of the applied geochemist is determined not only by the sensitivity of the colour-forming reagent but also by the size of the sample which can be taken without introducing extra time-consuming separations. Thus, a few parts per hundred-million of heavy metals (Pb, Cu, Zn) in natural water can be readily determined by evaluating the colour produced in the organic layer when a 50-ml. sample is shaken with a solution of dithizone in carbon tetrachloride and an appropriate buffer solution. On the other hand, in order to determine arsenic, tin or molybdenum in water, the elements must first be concentrated by distillation, the employment of ion-exchange resins or by means of collector precipitates, as the reagents available for their determination are far less sensitive than dithizone.

From the point of view of the applied geochemist the ideal colorimetric method should possess the following characteristics:

i. It should be capable of detecting one part per million of the element in question in a comparatively small quantity of soil or sediment. If it is designed for water analysis it should be capable of detecting a few parts per hundred million without preliminary concentrating operations.

ii. It should involve a minimum of operations and the apparatus should be of the simplest type. A source of heat should be unnecessary. That is to say, the ideal method would be one in which the sample was shaken with a single solution which resulted in a colour developing which could be readily evaluated.

iii. The reagents used should be stable under extreme climatic conditions, readily available in an acceptable state of purity, and comparatively cheap. They should also be innocuous.

iv. The reagent should be specific.

v. Standards should be permanent, and preferably solids for ease of transport.

At this point in time no method possesses all these characteristics. Heat has often to be employed to 'extract' the element from the sample: separations are often necessary: many of the reagents are unstable, whilst some have to be purified before use: some are distinctly poisonous and others are not readily obtainable: few of the reactions used are absolutely specific: often the standards are in a liquid form and have to be prepared daily, or, at least, at short intervals of time. Nevertheless, by developing completely new colorimetric methods and by 'stream-lining' old ones, many methods are now available which are generally highly reliable, and so simple and rapid that with a little training an intelligent individual, untrained in chemistry, can analyze from 50 to over a hundred samples per 8-hour day, even in a temporary field laboratory. The apparatus and techniques employed to achieve this high productivity are as follows:-

Samples are collected in resin-impregnated envelopes with metal ties and in hot climates these containers are opened and attached to a board to dry in the sun. (This ensures that should it commence to rain the samples can be rapidly removed to a dry place). Elsewhere the samples are dried in roasting pans containing a bed of sand over a Primus stove.

The dried sample, having been disintegrated by lightly hammering the envelope, is then passed through one or more Nylon screens in order to obtain the necessary fractions for analysis. Nylon screens are used in preference to metal in order to eliminate one possible source of contamination. Such screens may be made very easily (from, for example, shallow, cylindrical, wooden, crystallised-fruit boxes, having removed the top and base). Experience has shown that in the vast majority of cases analysis of the minus 80-mesh (B.S.S.) soil fraction yields satisfactory data for exploration purposes and hence sample grinding can normally be dispensed with.

In the field-laboratory soil or sediment for analysis is usually weighed on a 500 mg. torsion balance as it is only on rare occasions that more than 0·25g. aliquots are used. However, at the sacrifice of some accuracy a measured volume of the sample may be used. This can be obtained by filling, by a standardised procedure, a calibrated depression in a perspex 'block' measuring c. 3-in. x $\frac{1}{2}$-in. x $\frac{1}{2}$-in. A torsion balance is also used to measure small quantities of reagent accurately. When an approximate weight of a comparatively large quantity of solid reagent is needed a spring-balance, or one of the many robust, comparatively inaccurate, balances in common use in laboratories is used. Alternatively

appropriately calibrated beakers, crucibles, etc., may be used to obtain an approximate weight of a given solid.

Depending on the degree of accuracy required, volumes of liquid are measured by using calibrated measuring cylinders, calibrated test tubes (usually appropriately marked with a diamond pencil), graduated pipettes (usually fitted with an attachment so that the liquid can be drawn into the pipette and released from it without applying the apparatus to the lips), and dispensers which can be attached to polythene bottles, etc., and which are not unlike the apparatus used in bars to deliver a standard tot of whiskey.

A Primus, or similar type of stove, is the usual source of heat in the field, and by attaching a coronet to it six tubes can be treated simultaneously. Six or seven small nickel crucibles can also be heated at the same time by placing each in an appropriately-sized hole in a metal plate which is then clamped over the flame.

As filtering is a time-consuming process it is eliminated as far as possible; however, when it cannot be avoided an extraction stick is usually employed. This consists of a glass tube - several inches longer than the test tube into which it has to be inserted - constricted somewhat at a point about $1\frac{1}{2}$-in. from one end. The $1\frac{1}{2}$ in. length of tube is plugged with glass wool whilst a well-fitting cork is inserted into the other end. To separate liquid from solid the stick with its plugged end facing downwards, is placed in the test-tube containing the mixture, and the whole is heated in a water bath. (The water bath used in applied geochemical analysis consists of a squat litre-beaker - half-filled with water - in which is a metal stand capable of holding six tubes. As the apparatus is heated the air in the extraction stick expands and some of it passes through the plug, and after bubbles have been emerging freely from it for a few minutes the tube - still containing the extraction stick - is removed and allowed to cool. As the air in the stick contracts the atmospheric pressure forces liquid through the plug into it. The stick is then removed, inverted, and the filtrate transferred to another tube by removing the cork.

All reagents used are - whenever possible - of analytical grade, but, as on occasion sufficiently pure reagents are not obtainable from the suppliers some have to be purified. Often this involves the preparation of a solution of the reagent in question followed by a cleaning operation involving shaking it in a separatory funnel with a reagent capable of extracting components likely to interfere in the subsequent analysis. Cleaning operations are time-consuming and consequently considerable work has been devoted to modifying certain analytical methods so that all the reagent needed could be used as supplied by the manufacturer.

In order to avoid contamination all apparatus must have a final wash in metal-free water before use and only metal-free water must be used during the course of an analysis and in the preparation of aqueous solutions. This is, however, easily prepared in the field by passing 'ordinary' water slowly through a 'mixed-resin' column. In course of time the column ceases to be effective and so the water emerging from it is periodically checked to ensure that it is free from heavy metals by subjecting it to the same dithizone test which is used to determine heavy metals in natural waters. In the laboratory a more elaborate apparatus is used which enables the 'quality' of the emerging water to be gauged instantly by measuring its conductivity.

Some prefer to use only silica-glassware when carrying out geochemical analysis but experience teaches that no significant contamination accrues when ordinary laboratory glassware is used. Polythene containers, however, are to be recommended whenever they can be used as they are much less easily broken than glass ones: polythene wash-bottles are also much more convenient to use than their glass counterparts.

Finally, in the field all colour comparisons are made visually.

No further major pieces of apparatus are needed for the usual geochemical analysis involving the comparison of colours of liquids, but a few additions are necessary when employing the special colorimetric methods described below.

Special colorimetric methods.

Of the special colorimetric methods the paper chromatographic ones have been amongst the most widely used. They have been employed for the simultaneous determination of copper, cobalt and nickel, and also for the determination of uranium, lead, tantalum, niobium and lead (Hunt, North and Wells, 1955). In every case the method consists essentially in applying an aliquot of a suitable extract of a soil, or sediment, to one end of a filter-paper strip and allowing an organic solvent mixture to diffuse up through the test spot. The solvent is chosen to produce a separation of the desired metal, which is then detected by spraying the strip with a suitable reagent. The quantity of metal present is estimated by comparison with standard strips (Hunt, North and Wells, 1955, 172). A specially designed piece of Whatman No. 1 filter-paper is employed which permits ten samples to be analyzed simultaneously. Each piece of paper is a rectangular sheet (21·3 cm. x 11 cm.) in which eleven slots have been cut parallel to the short side so as to leave 12 strips joined top and bottom. An aliquot of sample solution (from 0·01 - 0·05 ml.) is placed near to one end of each strip excepting the first and last - these are left blank. The sheet is then dried somewhat and bent round to form a cylinder: a paper clip being used to hold the upper ends together. The cylinder is then placed vertically in a large beaker containing a 1 cm.-thick layer of solvent and the beaker is covered with a Petri dish. When the solvent has diffused up the strip to a point near the top of the slots the paper is removed and sprayed with a suitable developing reagent. The coloured spots are then compared with standards which have been similarly prepared. As the tantalum and niobium methods involve the use of hydrofluoric acid, polythene beakers have to be used instead of the usual glass ones.

The accuracy, sensitivity, simplicity and rapidity of chromatographic methods are such that they compare favourably with the 'normal' colorimetric ones, yet they are generally not used when one of the latter is available: perhaps this is due largely, or entirely, to the fact that 'normal' methods were developed first.

Reference has already been made to the employment of ion-exchange resins as a means of effecting a preliminary concentration of an element to be determined in natural waters: the writer (unpublished studies) has used the technique, for example, during his studies concerning the presence of tin in Cornish stream waters. Usually the impregnated resin is ashed at c. 550°C. and the residue is then analyzed in the same way as a soil sample. Preliminary concentration of

uranium from the waters of the River Fal, Cornwall, by means of resin was also used by Ostle (1954). He, however, completed the analysis in a somewhat novel way. The resin was ashed in a platinum dish and subsequently fused with a fixed weight of a standard flux. The fluorescence of the resultant phosphor - an exposure to ultraviolet light - was then compared with that of standards containing known amounts of uranium. In the field comparison was made by visual inspection, but in the laboratory more precise determinations were made by means of a fluorimeter.

On occasion, the analytical method can be simplified by separating the element of interest as a gaseous compound. Germanium, for example, is separated from leachates of appropriately treated samples of rock, soil, and coal ash as the chloride. Distillation of this compound is conveniently effected in a distillation rack on which six samples can be dealt with simultaneously. The element is finally converted to the germanium phenylfluorone complex and the analysis completed colorimetrically (Almond, Crowe and Thompson, 1955). The determination of arsenic in soils, etc., depends on the conversion of the element to arsine in a Gutzeit apparatus. This gas then passes over a confined disc of filter paper impregnated with mercuric chloride, and the colour of the reaction product (elemental arsenic) is subsequently compared with artificial standards (Almond, 1953).

Within a certain concentration range, and under strictly controlled conditions, the intensity of colour of a precipitate of a compound of a given element deposited on filter paper is a function of the concentration of the element in the test solution. Obviously the volume of test solution must be known, the area of paper on which the precipitate is deposited must be the same during the preparation of the standards and the analysis of 'unknowns', and the rate of precipitation must be strictly controlled. A number of pieces of apparatus, of varying degrees of simplicity, have been designed to meet these demands: all of them depend on drawing the test substance at a constant and reproducible rate through a disc of filter paper which is so damped that lateral migration is not possible. (See Footnote). The first of these to be given prominence was termed the chromograph and was designed and described by Stevens and Lakin (1949). These workers also evolved methods for the determination of nickel and copper in soils which depended on the use of the instrument (the nickel was deposited as the dimethylglyoxime complex and the copper as rubeanate). The apparatus, however, was not well received by Field workers: some regarded it as being too complex, and others too fragile. Subsequently a much simpler version has been developed by Martinet and Genin (1956) who have employed it to determine lead, copper, zinc and gold in soils.

On occasion unconfined spot methods have been used to obtain semi-quantitative geochemical data and though these are obviously not as satisfactory as the type just previously described they are not without merit as they are extremely simple and require very little apparatus. Warren and Delavault (1959) describe such a method which was used successfully to delineate a hitherto unknown copper deposit

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Footnote: In some analysis the precipitate is developed in the test solution and subsequently deposited on the paper, whilst in others the paper is impregnated with the precipitant and so precipitation takes place on its surface.

in the Craigmont area of Canada. These workers shake a given volume of soil with a sodium acetate/acetic acid buffer for 15 seconds and then pour the slurry into a filter paper cone which rests in a beaker. The tip of the cone just touches a square of filter paper impregnated with rubeanic acid. The copper ions which are carried through the cone react with the rubeanic acid forming a crudely circular precipitate of copper rubeanate. The colour and size of the 'spot' is then compared with standards.

Conclusion.

In this review the writer has confined himself to the analytical aspect of geochemical prospecting for metals. However, geochemical methods have also been used, particularly in the U.S.S.R., to facilitate the search for oil, and in this field many analytical methods not discussed in this paper are employed: these will form the subject of another review.

Since this paper was read to members of the Institute some new techniques, etc., have come into prominence: these have now been included.

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At the conclusion of the Address, Mr. J. P. R. Polkinghorne demonstrated the technique of determining copper and arsenic in soil.

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